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RAMAN SPECTRA OF PARA FLUOROTOLUENE AND PHENYL ACETONITRILE IN THE SOLID STATE AT −180°C*

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PLATE I

ABSTRACT. The Raman spectra of para fluorotoluene and phenyl acetonitrile have been studied in the liquid state and in the solid state at −180°C and the results have been compared with those reported by previous workers for a few compounds having similar molecules. In the case of para fluorotoluene a strong and broad new Raman line of Raman shift 103 cm^{-1} has been observed. The lines 152 cm^{-1} and 333 cm^{-1} are found to shift considerably with the solidification of the liquid.

In the case of phenyl acetonitrile the Raman line 361 cm^{-1} due to C ≡ N deformation oscillation is found to become very weak but the line 2250 cm^{-1} due to C ≡ N stretching oscillation remains almost unchanged when the liquid is solidified. Further, this compound in the solid state also produces only one new Raman line at 95 cm^{-1}. A strong and broad luminescence band at about 21198 cm^{-1} has also been observed in the spectrum due to the crystals in the solid state at −180°C. The significance of these changes has been discussed.

INTRODUCTION

Raman spectra of some substituted toluenes (Biswas, 1954; Sanyal, 1953) and a few nitriles (Bishui, 1948) in different states were studied in this laboratory and some interesting changes were observed in the spectra with solidification of the substances. In continuation of these investigations the Raman spectra of para fluorotoluene and phenyl acetonitrile in the liquid state and in the solid state at −180°C have been investigated and the results have been discussed in the light of the assignment of the lines made by previous workers.

EXPERIMENTAL

The chemicals used in the present investigation were of chemically pure quality. Para fluorotoluene was supplied by Eastman Kodak Co., U.S.A. and phenyl acetonitrile by Fischer Scientific Co., New York. The liquids were subjected to distillation under reduced pressure before each exposure. The spectro-

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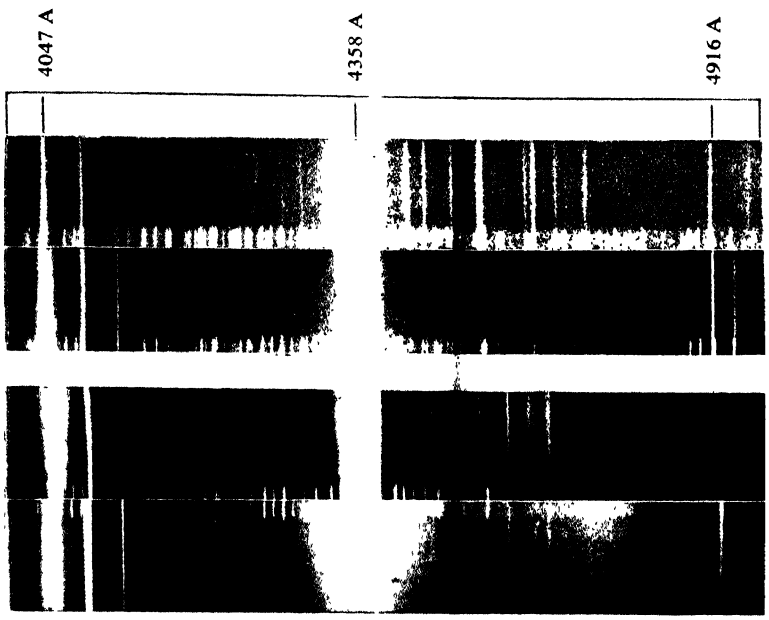

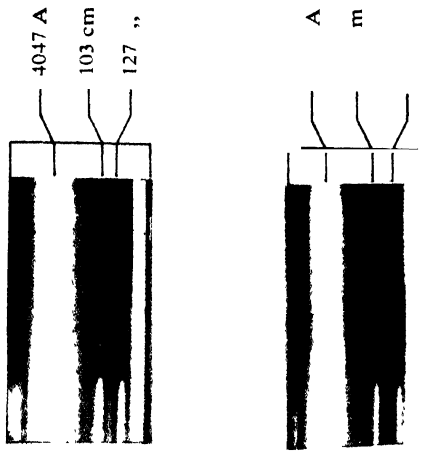

Fig. 3.

Fig. 1. *(a)* Raman spectra of para fluorotoluene liquid with filter at 28°C
(b) ,, ,, ,, ,, ,, solid at −180°C
Fig. 2. *(a)* Raman spectra of phenyl acetonitrile liquid at 28°C
(b) ,, ,, ,, ,, ,, solid at −180°C
Fig. 3. *(a)* Low frequency Raman lines of para fluorotoluene at −180°C
(b) ,, ,, ,, ,, ,, phenyl acetonitrile at −180°C

grams of the substances in the liquid and solid states and the polarised spectra were recorded with the same arrangements as those used previously (Deb, 1960). The spectra were photographed on Ilford Zenith plates using a Fuess glass spectrograph giving a dispersion of about 11 A per mm in the 4046 A region. The wavelengths were measured with the help of iron arc spectrum recorded on the same plate as a comparison.

RESULTS AND DISCUSSION

The spectrograms are reproduced in Plate I. The observed Raman frequencies together with those reported for the compounds in the liquid state by previous workers are tabulated in Table I and Table II. The polarised and totally depolarised lines are indicated by the letters P and D respectively.

Parafluorotoluene

(a) *Low-frequency lines*

It can be seen from Figs. 1(a) and 1(b) and Table I that in the solid state at $-180°C$, para fluorotoluene yields two new low frequency Raman lines with Raman frequencies 103 cm^{-1} and 127 cm^{-1} respectively. It was previously observed by Sanyal (1953) and Biswas (1954) that para chlorotoluene yields four such lines of Raman frequencies 30 cm^{-1}, 50 cm^{-1}, 85 cm^{-1} and 129 cm^{-1} respectively and para bromotoluene yields only three such lines of Raman frequencies 52 cm^{-1}, 94 cm^{-1} and 133 cm^{-1} respectively. A comparison of these results shows that the frequency about 130 cm^{-1} is present in all these three molecules in the solid state and the other two frequencies 50 and 85 cm^{-1} shown by para chlorotoluene do not change very much when the chlorine atom is replaced by the bromine atom. This shows that the atomic weight of the substituent halogen atoms has very little influence on the frequencies and therefore, they may not belong to any intermolecular vibration in which the adjacent molecules oscillate against each other in the lattice. It also appears that the number of low frequency lines is related very much to the chemical affinity of the molecules. Similar results were observed in the case of halogen substituted benzenes (Mukherjee, 1960). It has been suggested by some previous workers (Sirkar and Bishui, 1946; Sirkar, 1951) that these lines might be due to vibrations in groups of associated molecules in the solid state, but no attempt has been made to indicate the nature of such modes. The analysis of the results obtained with a large number of such compounds is necessary before such modes can be visualised.

(b) *Changes in the position of the other Raman lines with solidification.*

Ferguson *et al.* (1953) have reported the Raman and infrared spectra of para fluorotoluene and have analysed the vibrational bands assuming a point group D_{2h} for the molecule, because the effective mass of the fluorine atom is

nearly the same as that of the CH_3 group taken as a point mass. It can be seen from Table I that the line at 152 cm^{-1} of the liquid, assigned by them to a

TABLE I

Raman spectrum of *p*-fluorotoluene

Liquid		Solid at −180°C
Ferguson *et al.* (1953)	Present author	Present author
		103 (8b)
		127 (4)
152	152 (1b)D	
312	310 (1)P	
341	333 (10)D	353 (6)
425		
454	450 (10)P	456 (6)
502	498 (1)D	
638	638 (10)D	638 (6)
695	692 (2)P	
728	722 (2)P	
740		
825	819 (10)P	826 (5)
842	840 (10)P	844 (3)
908	910 (0)	
929		
1003	997 (1)	
1017		
1040		
1061		
1099		
1157	1153 (6)P	1153 (5)
1178		
1214	1214 (10)P	1219 (8)
1221		
1278		
1299	1298 (4) P	1296 (3)
1351		
1382	1380 (6) P	1383 (3)
1404		
1433		
1455	1455 (1b)P	
1495		
1508	1510 (0b)	
1601	1597 (6b)P	1597 (2)
1614		
1858		
1906		
1940		
2385		
2416		
2454		
2740	2736 (2)P	
2871	2876 (4)	
2928	2922 (6) P	2922 (2)
3071	3069 (8)P	3069 (3)

b_{2u} mode of the molecule representing probably an out-of-plane carbon bending vibration shifts to 127 cm^{-1} when the substance is solidified and cooled to −180°C. Also the line at 333 cm^{-1} due to a b_{3u} mode shifts under similar conditions to 353 cm^{-1}. In place of two lines at 1601 cm^{-1} and 1614 cm^{-1} observed by the above authors in the case of the liquid, a broad unresolved band at 1597 cm^{-1} is observed in the present investigation. This band, however, becomes sharp when the liquid is frozen. Further, the lines 450 cm^{-1}, 819 cm^{-1} and 840 cm^{-1} of the liquid shift respectively to 456 cm^{-1}, 826 cm^{-1} and 844 cm^{-1} when the liquid is frozen. All these changes suggest some sort of intermolecular association which affects the frequencies of some of the modes of vibration of the single molecule.

Phenyl acetonitrile

(a) *Low-frequency lines*

This compound yields only one low frequency Raman line at 95 cm^{-1} when the liquid is solidified and cooled to −180°C. Bishui (1948) studied Raman spectrum of benzonitrile at low temperature and he also observed only one such line at 94 cm^{-1}. A similar compound benzyl chloride, on the other hand, produces four such new lines of Raman shifts 46 cm^{-1}, 62 cm^{-1}, 82 cm^{-1} and 88 cm^{-1} respectively in the solid state at −180°C (Ray, 1951). These results again show that the number of low frequency lines produced by these compounds cannot be satisfactorily explained on the hypothesis of the angular oscillations of the molecules in the crystal lattice, because the number seems to depend on the nature of the individual substituents and not on their masses.

(b) *Changes in the other Raman lines*

In the solid state at −180°C, the line 361 cm^{-1} due to C ≡ N deformation oscillation of the molecule in the liquid becomes very weak, but the line 2250 cm^{-1} due to C ≡ N stretching oscillation remains almost unchanged. These changes are similar to those observed in the case of benzonitrile by Bishui (1948) who suggested that C ≡ N deformation oscillation might be restricted in the solid state due to association of the molecules. The results of the present investigation thus confirm this view . The lines 3059 cm^{-1} and 3065 cm^{-1} in the liquid state reported in Tables by Landolt-Börnstein (1951) are not resolved in the spectrograms obtained in the present case, but they appear as a broad band with its centre at 3065 cm^{-1}. With the solidification of the liquid, the band remains broad. Besides these changes mentioned above, frequencies of some other Raman lines of the single molecules are also affected slightly. All these changes again appear to point to the formation of associated groups of molecules in the frozen state of the nitrile compound at the low temperature.

(c) *Luminescence spectra*

In the Raman spectrum of phenyl acetonitrile in the solid state at −180°C a strong and broad luminescence band with its centre at 21198 cm^{-1} has been observed. It is well known now that some substituted benzenes at low temperatures produce such bands in the visible region (Kasha, 1952; Sirkar and Biswas,

TABLE I

Raman spectrum of phenyl acetonitrile

Liquid		Solid at −180°C
Landolt-Bornstein (1951)	Present author	Present author
		95 (6b)
126 (6)	132 (8b)D	132 (4)
216 (2sb)		
235 (3b)	238 (4b)D	243 (3)
322 (4)	324 (2)P	
358 (5)	361 (5)D	361 (0)
428 (3b)	432 (1b)P	
468 (1b)	482 (2b)P	482 (2)
618 (7)	621 (6)D	623 (3)
744 (2)	752 (0b)P	752 (2)
798 (6)	808 (6) P	
812 (6b)	820 (6)P	812 (4)
849 (1)		
991 (1)		
1003 (10)	1008 (12)P	1008 (8)
1031 (8)	1032 (6)P	1032 (2)
1157 (4)	1160 (2) P	
1188 (4)		
1192 (7)	1192 (8)P	1205 (4b)
1414 (5)	1419 (3)P	1416 (0)
1499 (0)		
1589 (5)	1591 (3)P	
1602 (6)	1602 (4)D	1599 (3b)
2252 (6)	2250 (10)P	2249 (6)
2914 (5b)	2920 (10)P	2923 (6)
2984 (3)		
3011 (3)		
3046 (3)		
3059 (9)		
3065 (8b)	3065 (10b)P	3062 (8b)

1956; Biswas, 1956a, 1956b) by triplet→singlet transition, but all disubstituted benzenes do not necessarily produce such luminescence in the visible region. Probably the wavelength of singlet→triplet absorption band of phenyl acetonitrile is longer than 3650Å group of mercury lines, and in other nitriles not showing such luminescence the absorption band may be at wavelengths shorter than the 3650Å group.

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